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ELECTRIC MICROFIELD DISTRIBUTION IN CHARGED FLUIDS: PLASMAS, IONIC AND DIPOLAR MIXTURES

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ABSTRACT

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1-INTRODUCTION

The recent revival of the interest in the study of the electric microfield distribution in charged plasmas has been motivated by the use of the broadening of spectral lines in very hot plasmas to measure can be used to measure the temperatures in fusion processes.

The study of the fluctuating electric microfields was pioneered by Holtsmark[1] [2] who studied the weak coupling limit.

A considerable advance was the application of the classical fluids methods for evaluating the electric microfield distribution in systems of point charges moving in a neutralizing background, a possibility, that was first suggested by Morita [3] and formulated in terms of correlation functions by Iglesias [4].The Morita-Iglesias formulation (MI in what follows) is a powerful tool for the study of the electric microfield and has prompted a number of investigations on the subject[5] [9]

In particular, in the last reference, Lado[9] discusses the use of the Mean Spherical Approximation (MSA) for the evaluation of the microfield in a one component plasma,as a starting point for employing the more accurate Hypernetted Chain (HNC) integral equation.

The electric microfield problem is also of interest in relation with different dense systems other than plasmas. The electric microfield distribution in solutions in general, and in ionic solutions in particular, is of interest in various branches in Chemical Physics, such as spectroscopy,light scattering, liquid state chemical kinetics, dielectrics and so on.

One of the objetives of this paper is, precisely to study the evaluation of the electric microfield distribution in systems composed of particles with

any shape, size and charge distribution.

For these systems we consider the distribution of the fluctuating field felt by a point in an object of finite size and with an arbritrary multipolar charge distribution.

We express it in terms of the multipolar expansion for the interaction energy between an imaginary dipole placed at the center of our test particle and the distribution of the charged particles in the system.

Our result is given in terms of quantities that can be computed by approximate liquid state theories. However, care must be taken because of the inconsistencies which are known to occur in these theories.

Because of the difficulties in simulating the electric microfield distribution in a molecular fluid,it is useful to know exact relations to estimate the accuracy of the approximations. The second moment of the microfield distribution can be evaluated for a charged object immersed in a plasma.This has led to the very succesful APEX theory for plasmas.[5] However,the second moment for our general case is much more complicated as we show in Section III, for a hard charged object of arbitrary shape in a fluid of charged hard spheres with point ions and dipoles, since it involves three body correlations.The point is, that in the Onsager limit [10 13],the three body terms cancel out, leaving a remarkably simple expression for the second moment of the electric microfield. In this strong coupling limit the field of every particle is completely screened out by the surroundings: This limit is equivalent to Onsager's procedure of immersing the test object into a conducting continuum media, so that the calculation of the internal energy becomes an exercise in electrostatics.

We illustrate these points with the application of the

mean spherical approximation to a mixture of ions and dipoles.

The layout of the paper is as follows. In the next section we formulate the microfield problem and introduce our model.We also give a generalization of the MI expressions for the molecular case,as an expansion in terms of electric multipoles.

In Section III we obtain an exact second moment relation for an arbitrary convex object immersed in a mixture of hard spherical ions and dipoles. In Section IV we discuss the strong coupling limits and make contact with Onsager's discussion[14].

Section V is devoted to mean spherical approximation calculations on ionic and dipolar fluids.Finally,in Section VI we make some general remarks and conclusions.

II-THE ELECTRIC MICROFIELD DISTRIBUTION

a) FORMULATION

Consider a mixture of s species of particles and let N_α be the number of particles of species α. The coordinates of particle i of species α are

$$\vec{X}_{\alpha i} = (\vec{R}_{\alpha i} , \hat{\Omega}_{\alpha i})$$

where $\vec{R}_{\alpha i}$ is a 3-dimensional vector which gives the position of the center of particle i and $\hat{\Omega}_{\alpha i} = (\psi, \theta, \phi)$

indicates the three Euler angles that determine the orientation of the particle. The electric field experienced at position $\vec{R}_0$ by an object immersed in the mixture is

$$\vec{E}_0 = \vec{E}(\vec{R}_0, \vec{X}^N) = \sum_{\alpha=1}^{s} \sum_{\alpha_i=1}^{N_\alpha} \vec{E}_{\alpha_i}(\vec{R}_{\alpha_i}, \hat{\Omega}_{\alpha_i}) \qquad (2.1)$$

Here $\vec{X}^N = (\vec{X}^{N_1} \ldots\ldots \vec{X}^{N_s})$ denotes the configuration of all the particles of the mixture.

The electric microfield distribution is in the MI formalism

$$W(\vec{\epsilon}) = \langle \delta(\vec{\epsilon} - \vec{E}) \rangle$$

$$= (1/8\pi^3) \int d\lambda \, e^{-i\vec{\lambda}.\vec{\epsilon}} \, A(\vec{\lambda}) \qquad (2.2)$$

with

$$A(\vec{\lambda}) = \langle e^{i\vec{\lambda}.\vec{E}_0} \rangle \qquad (2.3)$$

In these equations, the angular brackets denote the canonical ensemble average over the configuration of the N + 1 particles ($N = \sum_{\alpha=1}^{S} N_\alpha$) including the test object. We have also used the integral representation for the Dirac δ function and $i = \sqrt{-1}$,is the imaginary unity.

b) THE FOURIER TRANSFORM OF $W(\epsilon)$

If the system is isotropic, $A(\vec{\lambda})$, the Fourier transform of the microfield distribution, can be rewritten [4] (λ = magnitude of $\vec{\lambda}$) .

$$A(\lambda) = Q(\lambda)/Q(0)$$

$$= -\int_0^{\lambda} d\lambda' \, \partial \ln Q(\lambda')/\partial\lambda' \tag{2.4}$$

where

$$Q(\lambda) = \int d\vec{X}_0 d\vec{X}^{N} \, e^{-\beta V(\lambda)} \tag{2.5}$$

is the configuration partition function for a system interacting and the potential energy is complex

$$V(\lambda) = V - (i/\beta)\, \vec{\lambda}.\vec{E}_0 \tag{2.6}$$

Here V is the potential energy of the real system of N + 1 particles particles when $\lambda = 0$ and $\beta = (kT)^{-1}$ the usual Boltzmann factor.

Equations (2.4)- (2.5) can be expressed in the form of the free-energy integral in a coupling-process type calculation [3,4].

$$\ln A(\lambda) = (1/64\,\pi^4) \sum_{\alpha=1}^{S} \rho_\alpha \int d\lambda' \int d\hat{\Omega}_0 d\hat{\Omega}_1 \, d\hat{R}_{01} \left[i\lambda' . E_\alpha(\bar{X}_{01}) \; g_{0\alpha}^{\lambda}(0,1) \right] \tag{2.7}$$

The functions

$$g^{\lambda}_{0\alpha}(0,1)=g_{0\alpha}(\vec{R}_{01}\ \hat{\Omega}_0\hat{\Omega}_1;\hat{\Omega}_\lambda)$$

are pair distribution functions for a system with particles interacting with the complex potential given by Eq (2.6). Furthermore

$$g^{\lambda}_{0\alpha}(0,1)=[V^2/(Q(\lambda)](64\pi^4)\int dX_2\ \ldots\ dX_N\ e^{-\beta V(\lambda)} \qquad (2.8)$$

Here $\hat{\lambda}=\vec{\lambda}/\lambda$; $\hat{\Omega}_\lambda=i\hat{\lambda}$ and $\rho_\alpha=N_\alpha/V$

is the number density.

c) MULTIPOLE EXPANSION

To proceed we must define our model more precisely:

Our interaction is always parwise additive.

$$V=V(\vec{X}_0\ \vec{X}^N)=1/2\sum_{\alpha,\beta}^{S}\sum_{\alpha_i\neq\beta_j}^{N_\alpha,N_\beta}V_{\alpha\beta}(\alpha_i;\beta_j)+\sum_{\alpha=1}^{S}\sum_{\alpha_i=1}^{N_\alpha}V_{0\alpha}(0,\alpha_i) \qquad (2.9)$$

The pair potential $V_{\alpha\beta}(1,2)$ will have, in general a short ranged repulsive part and a long ranged electrostatic part:

$$V_{\alpha\beta}(1,2) = V^{(SR)}_{\alpha\beta}(1,2) + V^{(E)}_{\alpha\beta}(1,2) \qquad (2.10)$$

where the electrostatic part can be represented by a multipole expansion of the form[15 16]

$$V^{E}_{\alpha\beta}(1,2) = \sum_{m,n,l,\mu,\nu} v^{m,n,l}_{\alpha\beta,\mu,\nu}(R_{12})\, \Phi^{m,n,l}_{\mu,\nu}(1,2) \qquad (2.11)$$

Here $R_{12} = |\vec{R}_{12}|, \hat{R}_{12}$ which are the magnitude and direction of the vector $\vec{R}_{12} = \vec{R}_1 - \vec{R}_2$. The orientational dependence is contained in the rotational invariants

$$\Phi^{m,n,l}_{\mu,\nu'}(12) = \Phi^{m,n,l}_{\mu,\nu}(\hat{\Omega}_1, \hat{\Omega}_2, \hat{R}_{12}) =$$

$$= [(2m+1)(2n+1)]^{1/2} \sum_{\mu',\nu',\lambda',\mu,\nu,\lambda} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \\ \mu & \nu & \lambda \end{pmatrix} D^{m}_{\mu,\mu'}(\hat{\Omega}_1)\, D^{n}_{\nu,\nu'}(\hat{\Omega}_2)\, D^{l}_{\lambda,\lambda'}(\hat{R}_{12}) \qquad (2.12)$$

where the notation and conventions of ref. (17) for Wigner's generalized spherical harmonics and 3-J symbols have been used. The radial functions in Eq (2.11) are

$$v^{m,n,l}_{\alpha\beta}(R_{12}) = (-)^{m}[(2l+1)!/(2m+1)!(2n+1)!]^{1/2}\, Q^{m}_{\mu}(\alpha)\, Q^{n}_{\nu}(\beta)/R^{l+1}_{12} \qquad (2.13)$$

where $l = m+n$, and we have omitted the greek subindices to alleviate the notation. The electric multipoles are defined by

$$Q^{m}_{\mu}(\alpha) = \int_{\text{MOLECULE}} d\vec{r}\; r^{m} D^{m}_{\mu,\mu}(r)\; q_{\alpha}(\vec{r}) \qquad (2.14)$$

$q_\alpha(\vec{r})$ is the charge density distribution in the particle of species α.

We observe that the factor between brackets in the integrand of Eq. (2.7) can be expanded in a similar way:

$$i\,\hat{\lambda}.\vec{E}_\alpha(0,1) = \sum_{\nu} v^{1\,n\,n+1}_{0\alpha;1\nu}(R_{01})\,\Phi^{1\,n\,n+1}_{1\nu}(0,1) \qquad (2.15)$$

with

$$v^{1\,n\,n+1}_{0\alpha}(R_{01}) = -[(2n+3)(n+1)/3]^{1/2}\,Q^{n}_{\nu}(\alpha)/\,R^{n+2}_{01} \qquad (2.16)$$

The pair distributionfunction has the invariant expansion:

$$h^{\lambda}_{0\alpha}(0,1) = g^{\lambda}_{0\alpha}(0,1) - 1$$
$$- \sum_{\mu\nu}^{mn\ell} \Big[h^{mn\ell\,(r)}_{0\alpha;1\nu}(R_{01})\;\Phi^{mn\ell}_{\mu\nu}(\hat{\Omega}_0\hat{\Omega}_1\hat{R}_{01}) \Big]$$
$$+ h^{1\,n\,\ell\,(\lambda)}_{0\alpha;1\nu}(R_{01})\;\Phi^{1\,n\,\ell}_{0\nu}(\hat{\Omega}_0\hat{\Omega}_1\hat{R}_{01}) \qquad (2.17)$$

The superscript (r) indicates the functions which involve the real multipole distributions and (λ) those of the imaginary dipole. Because of the symmetry of the point dipole this last contains only invariants with $m = 1$, $\mu = 0$.

Substituting Eqs. (2.14)- (2.16) into Eq (2.7) we find, using the orthogonality properties of the rotational invariants

$$\ln A(\lambda) = -4\pi \sum_{\alpha=1}^{s} \rho_{\alpha} \sum_{n} [(n+1)/3(2n+3)]^{n} Q_{n}^{n}(\alpha) \int_{0}^{\lambda} d\lambda' \int_{0}^{\Omega} dR \; h_{n}^{n,n+1}(R_{n}) / R_{n}^{n} \qquad (2.18)$$

which is the generalization of the MI formula for a mixture of charged particles.

The integral is proportional to the energy of interaction between the imaginary dipole of the test object and the n-pole of a particle of type α.

It should be emphasized that, the 'origin' of the test object (i.e. the reference point for the multipoles Eq.(2.13)) is not necessarily at the centerof the particle.Our formalism, and in particular Eq (2.18) applies for the microfield distribution at any point of a given convex test object

It should be pointed out that the test object can be an extra particle or a particle belonging to one of the species in the mixture.

III-SECOND MOMENT FOR ION-DIPOLE MIXTURES

For the one component plasma of charged point particles in a neutralizing background, Jancovici[18] found that the second moment of the microfield distribution experienced for a test point particle is

$$< E_0^2 >= <\vec{E}_0 . \vec{E}_0>= 4\pi(\rho_b /\beta)(z/z_0) \tag{3.1}$$

where $\rho_b e$ (e=electron charge) is the background charge density, z and z_0 are the electrovalence of the plasma particles and of the test particle. The method used for the plasmas can be extended to calculate the second moment of the microfield distribution for a hard convex object of arbitrary shape ,charge $z_0 e$,immersed into a mixture of arbitrarily charged hard spheres. We assume that species α,of diameter σ_α , has charge $z_\alpha e$ ($= Q_0^0(\alpha)$) and also a point dipole $\vec{\mu}_\alpha = \mu_\alpha \hat{\Omega}_\alpha$ (with $\mu_\alpha = Q_0^1(\alpha)$).

The electrostatic part of the total potential is the sum of a short ranged part, $V^{(SR)}$ and the electrostatic part $V^{(E)}$ (2.10)

We have

$$V^{(E)}(\vec{X}_0 \vec{X}^{N'}) = z_0 e\, \phi(\vec{X}_0 \vec{X}^{N'}) - z_0 e \sum_{\alpha=1}^{s} \sum_{i=1}^{N_\alpha} \phi_{\alpha i}(0, q_i) \tag{3.2}$$

where $\phi_i(0, q_i)$ is the electrostatic potential generated in R_0 by particle i of species α.If our mixture consists only of charges and dipoles

$$\phi_{\alpha_i}(0,\alpha_i) = z_\alpha e/R_{0i} + \vec{\mu}\cdot(\hat{\Omega}_i \cdot \hat{R}_{0i})/R_{0i}^2 \qquad (3.3)$$

$\vec{E}_{0i}$ in Eq (2.1) verifies $\vec{E}_{\alpha_i} = -\vec{\nabla}_0 \phi_{\alpha_i}$ (with $\vec{\nabla}_0 = \vec{\nabla}_{R_0}$). Now

$$\langle \vec{E} \cdot \vec{E} \rangle = \langle \vec{\nabla} \phi \cdot \vec{\nabla} \phi \rangle \qquad (3.4)$$

Using the relation

$$-1/\beta\, \vec{\nabla}_0 e^{-\beta V} = -e^{-\beta V} [z_\alpha e \vec{\nabla} \phi + \vec{\nabla}_0 V^{(SR)}] \qquad (3.5)$$

we obtain

$$\langle E_0^2 \rangle = 1/Q \int d\vec{X}_0\, d\vec{X}^N\, (\vec{\nabla} \phi \cdot \vec{\nabla} \phi)\, e^{-\beta V}$$

$$= -1/Q\beta \sum_\alpha \int d\vec{X}_0\, d\vec{X}^N \{(\vec{\nabla}_0 \phi \cdot \vec{\nabla}_0 e^{-\beta V} + \beta e^{-\beta V} \vec{\nabla}_0 \phi \cdot \vec{\nabla}_0 V^{(SR)})\} \qquad (3.6)$$

In this equation $Q = Q(\lambda=0)$, where $Q(\lambda)$ is the partition function defined by Eq.(2.5) and $V^{(SR)}$ is the short ranged part of the total potential energy (in our case hard core interactions).

In the integral in (3.6) the first term is zero for a screening system, in which the field and potential are zero at the system boundaries. This can be shown using Green's theorem and Poisson's equation.

$$\nabla_0^2 \phi = -4\pi \sum_{\alpha=1}^{s} \sum_{\alpha_i=1}^{N_\alpha} z_\alpha e \, \delta(R_{0\alpha_i}) - \mu_{\alpha_i} [\hat{\Omega}_{\alpha_i} \cdot \vec{\nabla} \, \delta(R_{0\alpha_i})] \qquad (3.7)$$

$$= 0$$

Therefore

$$\langle E_0^2 \rangle = -1/(z_0 Q e) \int d\vec{X}_0 \, d\vec{X}^{N'} \, e^{-\beta V^{(N)}} \left(\vec{\nabla}_0 \phi_0 \cdot \vec{\nabla}_0 V^{(N)} \right) \qquad (3.8)$$

Now, since the media particles are hard, and the cavity particle is also hard and of arbritrary shape, the short ranged force is

$$e^{-\beta V^{(N)}} \vec{\nabla}_0 V^{(N)} = -1/\beta \, \vec{\nabla}_0 e^{-\beta V^{(N)}}$$

$$= -1/\beta \sum_{\alpha=1}^{s} \sum_{\alpha_i=1}^{N_\alpha} R_{0\alpha_i} \delta[\vec{R}_{0\alpha_i} - \sigma_{0\alpha_i}(\hat{\Omega}_0, \hat{R}_{0\alpha_i})] \qquad (3.9)$$

where $\sigma_{0\alpha_i}(\hat{\Omega}_0, \hat{R}_{0\alpha_i})$ is the distance of closest approach of i and 0, which depends on the orientations of $\hat{R}_{0\alpha_i}$, and $\hat{\Omega}_0$.

Using (3.3) and (3.9) in (3.8) we get

$$\langle E_0^2 \rangle = 1/(\beta \, z \, Q) \int d\vec{X}_0 \, d\vec{X}^{N'} \left(\sum_{\alpha=1}^{s} \sum_{\alpha_i=1}^{N_\alpha} \vec{\nabla}_0 \phi_{\alpha_i} \right) \cdot \left(\sum_{\beta=1}^{s} \sum_{\beta_j=1}^{N_\beta} \vec{n}(R_{0\beta_j}) \, \delta[R_{0\beta_j} - \sigma_{0\beta}(\hat{\Omega}_0, \hat{R}_{0\beta_j})] \right) \qquad (3.10).$$

where ϕ_{α_i} is the electrostatic potential due to particle α_i (3.3)

Separating the terms in which $\alpha_i = \beta_j$, we get

$$\langle E_0^2 \rangle = \langle E_0^2 \rangle_S + \langle E_0^2 \rangle_M \qquad (3.11)$$

The self term is

$$\langle E_0^2 \rangle_S = -kT/z_0 \int d\hat{\Omega}_1 \, d\hat{R}_{01} \sum_{\alpha=1}^{S} \rho_\alpha [\sigma_{0\alpha}(\hat{R}_{01}\ \hat{\Omega}_0)]\ \breve{n}(\hat{R}_{01})$$
$$\{ z_\alpha \hat{R}_{01} + \mu_\alpha/\sigma_{0\alpha}(\hat{R}_{01}\hat{\Omega}_0)[3\ (\hat{R}_{01}.\hat{\Omega}_1)\hat{R}_{01} - \hat{\Omega}_1] \} \qquad (3.12)$$

where the sum is over all species α in the system with charge $z_\alpha e$ and dipole moment μ_α. The function $\rho_\alpha[\sigma_{0\alpha}]$ is the contact probability density between the particle α and the test particle 0. It is a function of the angle $\hat{R}_{01}$ which gives the position of α relative to the test object 0. $\breve{n}(\hat{R}_{01})$ is the unit vector along the center to center distance when the particles are in contact. $\sigma_{0\alpha}(\hat{R}_{01}\hat{\Omega}_0)$ is the distance of closest approach for that orientation (see figure 1).

The mutual term is more complex

$$\langle E_0^2 \rangle_M = -kT/z_0 \int d\hat{\Omega}_1 \, d\hat{R}_{01} \, d\vec{X}_2 \sum_{\alpha\beta} \rho_{\alpha\beta}(1,2)|_{R_{01}=\sigma_{01}} [\sigma_{0\alpha}^2(\hat{R}_{01}\ \hat{\Omega}_0)]\ \breve{n}(\hat{R}_{01})$$
$$\{ z_\beta \hat{R}_{02} + \mu_\beta/R_{02}[\ 3\ (\hat{R}_{02}.\hat{\Omega}_2)R\ \ -\hat{\Omega}_2] \}/R_{02}^2 \qquad (3.13)$$

which is the average of field in the $(\breve{n}\ (\hat{R}_{01}))$ direction when particle 1 (of species α) is in contact with the test particle. This is a complicated term because it involves, a 3 body correlation function (particles 0, 1, 2) . However, in the Onsager limit, in which the fields outside of the test particle are completely screened out, this term should be be zero, and we get

$$\langle E_0^2 \rangle = \langle E_0^2 \rangle_S \qquad (3.14)$$

where $\langle E_0^2 \rangle_S$ is given by (3.12). In the case of a spherical test object in in a ionic mixture, we get

$$\langle E_0^2 \rangle\ = -4\pi/(\beta\ z_0\ \epsilon) \sum_{\alpha=1}^{s-1} \rho_\alpha\ z_\alpha\ g_{0\alpha}(\sigma_{0\alpha}) \qquad (3.15)$$

IV-THE ONSAGER LIMIT

In his classic paper of 1939, Onsager[14] considered the problem of calculating an exact lower bound for the interaction energy V of a neutral system composed of charged hard particles. Onsager solved the problem by immersing the impenetrable particles in an infinite conducting fluid, thereby obtaining the 'Onsager state' for which

$$V \geq V^{(ONSAGER)} = \sum_{\alpha} N_{\alpha} U_{\alpha} - \sum_{\alpha} N_{\alpha} U_{\alpha;self}^{(\Sigma)} \tag{4.1}$$

where U_{α} (the Onsager proper energy of one particle of species α) is the self energy (relative to the self energy of the original charges) of the 'Onsager atom'. This object is the original hard sphere with the original charge plus that surface charge induced on the sphere surface by the conducting boundary condition. Therefore $U_{\alpha;self}^{(\Sigma)}$ is the self energy of the (induced) surface charge.

Onsager's approach is valid also for point charges in non-hard core particles (e.g. the one-component plasma) as long as the particles distribution features pair-excluded regions (i.e. 'effective' hard core) [10 19]

Recent work showed [10 13 20 25] that the'Onsager state 'provides the exact description of the asymptotic strong coupling limit (e.g. T→0) of the solutions of both,the mean spherical approximation (MSA) and hypernetted chain

(HNC) integral equations for arbritrary hard particles. In particular, $V^{(ONSAGER)}$ which is the sum of individual terms, one for each particle in the system, is the exact strong coupling limiting energy as obtained from the solution of the MSA and HNC equations. The corresponding asymptotic direct correlation functions are given by the electrostatic interaction between the (induced) surface charges on the different particles.

Like the general formalism (Sec II) and the particular MSA formalism (Sec V below), the electrostatics involved in the 'Onsager State' can be developed for both real and complex charges. In particular, relations like (b.7) in appendix B follow immediately from the Onsager limit state due to the simple meaning of the direct correlation function as stated above.

Consider the microfield distribution problem in the Onsager limit. Denoting by $F(\lambda)=-kT \ln Q(\lambda)$ the excess configurational free energy of the system when the imaginary test point dipole is acting on the test object point, where the electric microfield is to be considered, then Eq(2.4) yields

$$\ln A(\lambda) = -\beta \left[F(\lambda)-F(\lambda=0)\right] \qquad (4.2)$$

In the strong coupling limit, the system approach to Onsager state in which the test object is immersed in a continuous conducting medium. Then the free energy difference in Eq (4.2) is

$$\ln A(\lambda)\Big|_{ONSAGER} = -\beta \left[U(\lambda)-U(\lambda=0)\right] \qquad (4.3)$$

where (see Fig 2a) $U_o(\lambda)$ is the self energy of the 'Onsager atom' corresponding to the test particle, with the imaginary dipole $i\lambda/\beta$ placed at the considered point, when it is immersed in the conducting medium. Since we have to average over all the orientations of λ, then the energy difference (4.3) is proportional to the square of the dipole strength λ:

$$\ln A(\lambda)\Big|_{\text{ONSAGER}} = \lambda^2/\beta \, \langle U_{\vec{\mu}=\vec{1}} \rangle_{\hat{\Omega}_\mu} \qquad (4.4)$$

Here $U_{\vec{\mu}=\vec{1}}$ is the Onsager proper energy (see above) of a hard particle, having the shape of the test object and with a real unit dipole which is placed at the test point (see Fig. 2b). $\langle \rangle_{\hat{\Omega}_\mu}$ denotes the average over the direction of the dipole $\vec{\mu}$ in a frame fixed to the test particle.

Thus the Onsager state, as well as the strong coupling solutions of the MSA and HNC equations, predict a Gaussian distribution for the electric microfield at any point inside the test object. The second moment depends only on the shape of the particle and the position of the test point, independent of the charge distribution inside the test object. It is given by

$$m_2 = \langle E_o^2 \rangle \xrightarrow[\text{LIMIT}]{\text{ONSAGER}} -6kT \, \langle U_{\vec{\mu}=\vec{1}} \rangle_{\hat{\Omega}_{\mu'}} \qquad (4.5)$$

The Onsager self energy for a dipole μ at the center of a sphere of radius R is $-(1/2)\mu^2/R$.

For example, when the unit dipole (i.e. the test point) is placed at the center of a spherical particle of radius $r = \sigma/2$, we obtain regardless of the original charge distribution of the system,

$$\langle E_0^2 \rangle_{\text{ONSAGER}} = 3/(\beta r^3) = 24/(\beta \sigma^3) \tag{4.6}$$

For a multicomponent plasma at a charged point of charge $z_0 e$, the Wigner-Seitz ion sphere radius is $a_{ws}\left(z_0/\langle z\rangle\right)^{1/3}$, where $\langle z\rangle$ is the mean electrovalence . Then the exact second moment Eq (3.1) is recovered:

$$\begin{aligned}\langle E_0^2 \rangle_{\text{ONSAGER}} &= 3/(\beta a_{ws}^3)(\langle z\rangle/z_0) \\ &= 4\pi \rho_B \langle z\rangle/\beta z_0\end{aligned} \tag{4.7}$$

Now using e/a_{ws}^2 as the unit of electric field ($\Gamma_0 = \beta e^2/a_{ws}$) we get

$$\langle E_0^2 \rangle_{\text{ONSAGER}} = 3/(\Gamma_0)(z_0/\langle z\rangle) \tag{4.8}$$

V THE MEAN SPHERICAL APPROXIMATION

The general formalism of the microfield distribution developed in Section III is suited to integral equations techniques. The appropiate Ornstein-Zernike (O.Z.) equation for the fluid in the presence of the test particle λ [26]

$$h_{o\alpha}(\vec{R}_{01}\,\hat{\Omega}_0\,\hat{\Omega}_1;\hat{\Omega}_\lambda) - c_{o\alpha}(\vec{R}_{01}\,\hat{\Omega}_0 \quad \hat{\Omega}_1;\hat{\Omega}_\lambda)$$
$$= \sum_{\beta=1}^{s} \frac{\rho_\beta}{8\pi^2}\int d\vec{R}_{31}\,d\hat{\Omega}_3\, h_{o\beta}(\vec{R}_{03}\,\hat{\Omega}_0 \quad \hat{\Omega}_3;\hat{\Omega}_\lambda)\, c_{\beta\alpha}(\vec{R}_{31}\,\hat{\Omega}_3\,\hat{\Omega}_1;\hat{\Omega}_\lambda)$$
$$+\frac{\rho_o}{8\pi^2}\int d\vec{R}_{31}\,d\hat{\Omega}_3\, h_{oo}(\vec{R}_{03}\,\hat{\Omega}_0 \quad \hat{\Omega}_3;\hat{\Omega}_\lambda)\, c_{o\alpha}(\vec{R}_{31}\,\hat{\Omega}_3 \quad \hat{\Omega}_1;\hat{\Omega}_\lambda) \tag{5.1}$$

where $c_{\alpha\beta}$ ($\alpha, \beta = 0,1,\ldots.s$) is the direct correlation function. In Eq (5.1) we have included the test object as member of a new species with number density $N_o / V = \rho_o$. Eventually we will take the limit, $N_o \to 1$ (or in the thermodynamic limit, $\rho_o \to 0$).

The Ornstein-Zernike equation can be closed by several approximate forms of the direct correlation function. The simplest of such closures is the mean spherical approximation [27]. The particles are hard particles, so that

$$g_{\alpha\beta}(\vec{X}_1\,\vec{X}_2) = 0 \qquad R_{12} < \sigma_{\alpha\beta} \quad \text{(exact)} \tag{5.2}$$

$$c_{\alpha\beta}(\vec{X}_1 \vec{X}_2) = -\beta V_{\alpha\beta}(\vec{X}_1 \vec{X}_2) \qquad R_{12} > \sigma_{\alpha\beta} \tag{5.3}$$

where $\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta) / 2$; σ_α is the diameter of species α and $V_{\alpha\beta}$ is the pair potential.

The general solution of Eq.(5.1) with the closures (5.2) (5.3), for arbritrary multipolar expansions [28] [29], shows that, because of the linearity of the MSA, the R-integrals in Eq (2.18) are proportional to the imaginary dipole strength.

$$\int dR_{01} h_{0\alpha;0\nu}(R_{01}) / R_{01}^{n} \propto \lambda \tag{5.4}$$

Then, we see that in the MSA the Fourier transform of the microfield distribution is Gaussian

$$\ln A(\lambda) = -1/6\, m_2 \lambda^2 \tag{5.5}$$

where $m_2 = \langle E_0^2 \rangle$, the second moment of the distribution, depends on the particular multipolar density expansion and the diameter of the particles as well as on the multipoles and diameter of the test object.

We can take advantage of the availability of analytical solutions of the MSA for some particular models in order to obtain explicitly their second moments

Lado[9] has recently considered the microfield problem in the MSA for a one component plasma of point charged particles in a neutralizing background . In this work we study a larger class of systems:

a) Mixture of charged hard spheres (primitive model of electrolyte)

b) One component system of dipolar hard spheres and

c) Mixture of charged hard spheres and dipolar hard spheres(non-primitive model of electrolyte).

For these systems we study in particular the strong coupling limit of the Onsager states. We will restrict ourselves to the special case in which the test object is one of the particles of the system and will consider only the microfield at the sphere center.

a)PRIMITIVE MODEL OF ELECTROLYTES

The system is a mixture of s-1 species of hard spheres of diameter σ_α with a point charge $z_\alpha e$ located at the center and number density $\rho_\alpha (\alpha = 1.....s-1)$. The solvent is treated as a structureless continuum with a dielectric constant ϵ.

The electric field felt by a test particle of type γ with $\sigma_\gamma = \sigma_0$ and $z_\gamma = z_0$ located at R is,at the center of the sphere

$$\vec{E}_o = -\sum_{\alpha=1}^{s-1} \sum_{i=1}^{n_\alpha} \left(z_\alpha e / \epsilon R^2_{o\alpha i} \right) \hat{R}_{o\alpha i} \tag{5.6}$$

The correlation function which involve the test particle (labelled o) has the form (see Eq (2.17))

$$f^{\lambda}_{o\alpha}(\vec{R}_{o1}; \hat{\Omega}_\lambda) = f^{000}_{o\alpha}{}^{(r)}(R_{o1}) + f^{101}_{o\alpha}{}^{(\lambda)}(R_{o1}) \; [i \hat{\Omega}_\lambda \cdot \hat{R}_{o1}] \tag{5.7}$$

where f denotes h and c in the Ornstein Zernike equation (5.1).

Then Eq (2.7) yields (see also Eq (2.18))

$$\ln A(\lambda) = -4\pi/3 \left(e/\epsilon\right) \sum_{\alpha=1}^{s-1} \rho_\alpha z_\alpha \int_0^\lambda d\lambda' \int_{\sigma_{o\alpha}}^{\infty} dR \; h^{101}_{o\alpha}{}^{(\lambda')}(R_{o1}) \tag{5.8}$$

As shown by Lado[9] for plasmas(see Appendix B),if we solve the Ornstein Zernike equation (5.1) in the limit $\rho_s \to 0$ in the MSA ,then

$$f^{101}_{o\alpha}(R_{o1}) = \lambda/(\beta z_o e) \; df^{000}_{o\alpha}(R_{o1})/dR_{o1} \qquad (\alpha = 1, \ldots, s-1) \tag{5.9}$$

Here $f^{000}_{\gamma\alpha}(R_{o1}) - f^{000}_{o\alpha}{}^{(r)}(R_{o1})$ is the correlation function for the unperturbed (without the imaginary dipole) fluid.

Using Eq (5.9) for $h^{101}_{o\alpha}{}^{(\lambda)}$ and taking into account the electroneutrality condition we obtain Eq (5.5) with

$$m_2 = -4\pi/(\beta z_o \epsilon) \sum_{\alpha=1}^{s-1} \rho_\alpha z_\alpha g_{o\alpha}(\sigma_{o\alpha}) \tag{5.10}$$

where $g_{\sigma_{0\alpha}}(\sigma_{0\alpha})$ is the contact value of the pair distribution function for the primitive model of an electrolyte in the MSA.

Comparison of this second moment with the exact result given by (3.11) shows that the MSA has only the self contribution $\langle E_0^2 \rangle_s$ and does not have the mutual term $\langle E_0^2 \rangle_m$ .This is to be expected, since the MSA is an improved Onsager bound,should not have this term,which, anyway vanishes in the high coupling limit.

If we use the MSA result of the contact pair correlation function to compute the limiting form of m in the high coupling regime,we find that it diverges.This is a consequence of the well known inconsistency of the MSA,in which the correlations of opositely charged ions go to $-\infty$ rather than to zero.

An alternate way to compute the Onsager limit of the second moment m_2 is to include the test particle as a new species,with an imaginary dipole.Our system consists then of s-1 species plus a new kind of particle of species γ but with an additional imaginary dipole.For this system the energy parameter

$$\int_{\sigma_{0\alpha}}^{\infty} dR\, h_{0\alpha}^{101(\lambda)}(R)$$

is known in closed form in the MSA[29 34].The result is proportional to λ/β. Taking the limit $\rho_0 \to 0$, the energy integrals of our eq. (5.8) converges.

We see, then , that in the strong coupling limit the correct Onsager limit (4.6) is obtained.However we must use the energy route to obtain our results, because of the well known inconsistency of the MSA.

b) HARD DIPOLE FLUID

Consider now a collection of hard spheres of diameter σ with an embedded point dipole μ .We compute the microfield distribution at the center of these particles.The field generated by a particle at the center of the test particle 0 is

$$\vec{E}_0 = -\sum_{j=1}^{N_s} \mu_s / R_{0j}^3 \cdot [3\hat{R}_{0j} \cdot (\hat{R}_{0j} \cdot \hat{\Omega}_j \cdot)] \tag{5.11}$$

The relevant correlations are

$$h_{0s}^{\lambda}(\vec{X}_0 \vec{X}_1) = h_{0s}^{000(\sigma)}(R_{01}) + \sum_{\gamma=r,\lambda} \left\{ h_{0s}^{110(\gamma)}(R_{01})\ \Phi^{110}(\hat{\Omega}_0 \hat{\Omega} \hat{R}_{01}) + h_{0s}^{112(\gamma)}(R_{01})\ \Phi^{112}(\hat{\Omega}_0 \hat{\Omega} \hat{R}_{01}) \right\} \tag{5.12}$$

From (2.7) (and also from (2.18)) we have

$$\ln A(\lambda) = -4\pi \sqrt{2/15}\ \rho_s \mu_s \int_0^{\lambda} d\lambda' \int_{\sigma_{0s}}^{\infty} dR_{01} h^{112(\lambda')}(R_{01}) / R_{01} \tag{5.13}$$

As shown in appendix B ,the radial coefficients $h_{0s}^{110(\lambda)}(R_{01})$ and $h_{0s}^{112(\lambda)}(R_{01})$ in (5.12) are related to the ordinary (unperturbed) radial coefficients $h_{0s}^{110(\sigma)}(R_{01}) = h_{ss}^{110}(R_{01})$ and $h_{0s}^{112(\sigma)}(R_{01}) = h_{ss}^{112}(R_{01})$, by

$$h_{0s}^{110(\lambda)}(R_{01}) = -(\lambda/\beta \mu_s)\ h_{ss}^{110}(R_{01})$$
$$h_{0s}^{112(\lambda)}(R_{01}) = -(\lambda/\beta \mu_s)\ h_{ss}^{112}(R_{01}) \tag{5.14}$$

Again, we obtain the Gaussian microfield distribution with the second moment given by

$$m_2 = 4\, b_2/(3\beta\, \sigma_s^3) \tag{5.15}$$

The dipole-dipole energy parameter is

$$b_2 = -3\pi \sqrt{2/15}\, \rho_s\, \sigma_s^3 \int_{\sigma_s}^{\infty} dR\; h_{ss}^{112}(R)/R \tag{5.16}$$

and which can be calculated solving the Wertheim[32] equation

$$\frac{(1+b_2/3)^2}{(1-b_2/6)^4} - \frac{(1-b_2/6)^2}{(1+b_2/12)^4} = (4/3)\pi\, \beta\, \rho_s\, \mu_s^2 = d_2^2 \tag{5.17}$$

In the strong coupling limit $d_2^2 \to \infty$ and $b_2 \to 6$.

Indeed, the Onsager limits are also verified in this case.

c) ION DIPOLE MIXTURE

Consider now a mixture of s-1 different species of charged hard spheres of diameter σ_α, charge $z_\alpha e$ and number density $\rho_\alpha = N_\alpha/V$ and the solvent which has a diameter σ_s and dipole moment μ_s

The field at the center of the test particle is the sum of the ionic and dipolar contributions, given by (5.6) and (5.11). On the other hand the relevant correlation functions now are $h_{0\alpha}^{\lambda}(\vec{R}_\alpha\, \hat{\Omega}_\lambda)$ (5.7) and $h_{0s}^{\lambda}(\vec{X}_0, \vec{X}_1)$ (5.12). The microfield is

$$\ln A(\lambda) = -4\pi (e/3) \sum_{\alpha=1}^{s-1} \rho_\alpha z_\alpha \int_0^\lambda d\lambda' \int_{\sigma_{0\alpha}}^\infty dR_{01}\, h_{0\alpha}^{101(\lambda')}(R_{01})$$
$$+4\pi\sqrt{2/15}\ \rho_s \mu_s \int_0^\lambda d\lambda' \int_{\sigma_{0s}}^\infty dR_{01}\, h_{0s}^{112(\lambda')}(R_{01})/R_{01} \qquad (5.18)$$

Now we have to discuss two possibilities: i) the test particle is a dipole of the mixture, and ii) it is an ion of the mixture.

i) TEST DIPOLE

Following the steps that led to (5.14) (see also appendix B)

$$h_{0\alpha}^{101(\lambda)}(R_{01}) = -(\lambda/\beta\ \mu_s)\ h_{s\alpha}^{101}(R_{01}) \quad \alpha=1,..,s-1$$
$$h_{0s}^{110(\lambda)}(R_{01}) = -(\lambda/\beta\ \mu_s)\ h_{ss}^{110}(R_{01})$$
$$h_{ss}^{112(\lambda)}(R_{01}) = -(\lambda/\beta\ \mu_s)\ h_{ss}^{112}(R_{01}) \qquad (5.19)$$

From (5.18) we obtain again a gaussian (5.5) with m_2 expressed in terms of the ion-dipole and dipole-dipole energy parameters of the MSA of the ion-dipole mixture[33 34]

$$m_2 = 4/\beta\ [b_1/2\sqrt{3} + b_2/3\sigma_s^3] \qquad (5.20)$$

here

$$b_1 = -2\pi/\sqrt{3} \sum_{\alpha=1}^{s-1} \rho_\alpha z_\alpha e \int_{\sigma_{0\alpha}}^\infty dR\ h_{0\alpha}^{101}(R)$$

and b_2 is defined by (5.16). These parameters can be computed solving a system of three nonlinear algebraic equations.

ii) TEST CHARGE

If the test particle is an ion then we again use the method

of defining an extra species λ of diameter σ, charge z e and imaginary point dipole of strength $-i\lambda/\beta$. We now let the density of this hypothetical component go to zero. Eq. (5.18) yields

$$\ln A(\lambda) = -4/(3\beta) \int_0^{\lambda} d\lambda' \left[b_1(\lambda')/2\sqrt{3} + b_2(\lambda')/2\sigma_s^3 \right] \tag{5.21}$$

The calculation of b_1 and b_2 as functions of λ is identical to the case of the real dipole, and is described elsewhere[33 34]. The important point is that in the MSA, $b_1(\lambda)$ and $b_2(\lambda)$ are linear functions of λ . Therefore, we obtain again the Gaussian distribution (5.5).

VI-CONCLUSIONS

In this paper we discuss the microfield of a ionic solution in a molecular solvent.We extend the Morita-Iglesias formalism to include angular dependent interactions.

The mean spherical approximation yields a simple answer for the microfield in all the cases that were investigated:The primitive model of ionic solutions, the pure dipolar fluid and the ion-dipole mixture. For all of these cases the distribution is a Gaussian.The width of these Gaussians (which is the inverse of the second moment) can be obtained in two forms:

i) in terms of the contact probability . This form agrees, in the Onsager limit, with the limiting form of the exact value ,also derived in this paper.

ii) in terms of the excess energy parameter.

An interesting situation arises here: In the Onsager limit, the MSA contact probability of the ions diverges. So that although formally the MSA gives the correct limiting expression of the second moment in terms of the contact probabilities, the limit itself is incorrect.
The energy route (ii), however, leads to the correct limiting value of the second moment in the Onsager limit.This is probably a consequence of the well known inconsistency of the MSA.

Similarly to the situation for plasmas[9] the MSA should serve as a starting point for a more accurate integral equation treatment.In this treatment the Onsager gaussian result (4.4),(4.5) is the exact high coupling limit.

APPENDIX A

ONSAGER ENERGY FOR A DIPOLE IN A SPHERICAL CAVITY

Following Rosenfeld and Blum[12 13] we write the Onsager energy of an arbitrarily charged object immersed in a conducting medium

$$U_i^{ONSAGER} = -\frac{1}{2}\int_{\Sigma} d\bar{s}\ \phi_{i;1}(s)\,\sigma(s) \tag{a.1}$$

=-[self energy of the surface charge distribution $\sigma(s)$]

Here $\phi_{i;1}(s)$ is the potential due to the induced charges at the surface Σ. For a spherical object with a unit dipole at the center (and pointing in the direction of the z axis) we have

$$\phi_{i;1}(s) = -\cos\theta/r^2 \tag{a.2}$$

and

$$\sigma(s) = -\frac{3}{4\pi}\cos\theta/r^3 \tag{a.3}$$

where θ is the angle between the normal to the surface and the z axis. Then $U_{\vec{\mu}=\vec{1}}$ is given by

$$U_{\vec{\mu}=\vec{1}} = U_i^{ONSAGER} = -\frac{1}{2}r^3 \tag{a.4}$$

Finally, from (a.4) and (4.5) we get (4.6).

APPENDIX B

CORRELATION FUNCTIONS IN THE MSA

Consider the Ornstein-Zernike equation (5.1) in the limit $\rho_o \to 0$ We use the invariant expansion (2.17) for all the correlation functions. Then, using the transforms[28 29]

$$\tilde{F}^{mn\ell(\gamma)}_{o\alpha;\chi}(k) = \sum_{\ell} (-)^{\chi} \binom{mn\ell}{\chi - \chi_0} 4\pi i^{\ell} \int_0^{\infty} dR_{o1}\, R_{o1}^2\, j_{\ell}(kR_{o1})\, F^{mn\ell(\gamma)}_{o\alpha}(R_{o1}) \tag{b.1}$$

where $j_\ell(kR)$ is the spherical Bessel function of order 1, and $\tilde{F}$ is a generic notation for either $\tilde{C}$ or $\tilde{H}$ (transforms of c or h). The Ornstein-Zernike equation is

$$\tilde{H}^{mn(\gamma)}_{o\alpha;\chi}(k) - \tilde{C}^{mn(\gamma)}_{o\alpha;\chi}(k) = \sum_{\beta=1}^{s} \rho_\beta \sum_{n_1} \tilde{H}^{mn_1(\gamma)}_{o\beta}(k)\, \tilde{C}^{n_1 n}_{\beta\alpha}(k) \tag{b.2}$$

The Ornstein Zernike equation can be transformed to real space: Using the inverse transform of (b.1)

$$F^{mn(\gamma)}_{\alpha\beta;\chi}(R) = \frac{4\pi}{(2\pi)^{3/2}} \frac{1}{12} \int_0^{\infty} k \begin{Bmatrix} \sin(kR) \\ i\cos(kR) \end{Bmatrix} \tilde{F}^{mn|\gamma|}_{\alpha\beta;\chi}(k)\, dk \tag{b.3}$$

where the upper sin kR is for m+n even, and the lower cos kR is for m+n odd.

We analize now the case of the microfield at the center of one of the ions of the mixture, and at the center of a hard dipole, which could be in a ion-dipole mixture or a pure dipolar fluid.

a) TEST ION IN THE PRIMITIVE MODEL

Using (5.7), together with (b.1) and (b.3) in the Ornstein-Zernike equation (b.2) yields

$$\mathcal{H}_{o\alpha}^{00(\gamma)}(R) - \mathcal{C}_{o\alpha}^{00(\gamma)}(R) = \frac{2\pi}{R} \sum_{\rho=1}^{s-1} \rho_\rho \int_0^\infty dt\, t\, \mathcal{C}_{\rho\alpha}^{00}(t) \int_{|t-R|}^{t+R} ds\, s\, \mathcal{H}_{o\rho}^{00(\gamma)}(s) \tag{b.4}$$

and

$$\mathcal{H}_{o\alpha}^{10(\lambda)}(R) - \mathcal{C}_{o\alpha}^{10(\lambda)}(R) = \frac{2\pi}{R} \sum_{\rho=1}^{s-1} \rho_\rho \int_0^\infty dt\, t\, \mathcal{C}_{\rho\alpha}^{00}(t) \int_{R-t}^{t+R} ds\, s\, \mathcal{H}_{o\rho}^{00(\gamma)}(s) \tag{b.5}$$

The observation is that the MSA closure relations (5.2) and (5.3) yield

$$h_{o\alpha}^{101(\lambda)}(R) = 0 = \frac{\lambda}{\rho e z_o} \frac{d\, h_{o\alpha}^{000(\gamma)}(R)}{dR} \qquad R < \sigma_{o\alpha} \tag{b.6}$$

$$C_{o\alpha}^{101(\lambda)}(R) = \frac{\lambda z_\alpha e}{R^2} = \frac{\lambda}{\rho e z_o} \frac{d\, C_{o\alpha}^{000(\gamma)}(R)}{dR} \qquad R > \sigma_{o\alpha} \tag{b.7}$$

Then, defining

$$f_{o\alpha}^{101(\lambda)}(R) = \frac{\lambda}{\rho e z_o} \frac{d\, f_{o\alpha}^{000(\gamma)}(R)}{dR} \tag{b.8}$$

for all R, and using the fact that $f_{o\alpha}^{000(\gamma)}(R) = \mathcal{F}_{o\alpha}^{00(\gamma)}(R)$ we have

$$\mathcal{F}_{o\alpha}^{10(\lambda)}(R) = -\frac{1}{\sqrt{3}} \frac{\lambda}{\rho e z_o} \frac{1}{R} \frac{d}{dR} \left[R\, \mathcal{F}_{o\alpha}^{00(\gamma)}(R) \right] \tag{b.9}$$

so that if $\mathcal{F}_{o\alpha}^{00(\gamma)}(R)$ verifies (b.4), then $\mathcal{F}_{o\alpha}^{10(\lambda)}(R)$ defined by (b.9) should verify (b.5). Therefore, $f_{o\alpha}^{101(\lambda)}(R)$ as given by (b.8) is the solution of the problem. We also notice that $f_{o\alpha}^{000(\gamma)}(R)$ is equal to $f_{\gamma\alpha}^{000}(R)$ for the bulk unperturbed system (λ=0) when the test particle belongs to species γ.

b)TEST DIPOLE IN AN ION-DIPOLE MIXTURE

For this case the one dimensional projection of the Ornstein-Zernike equation yields (γ=r,λ)

$$\mathcal{H}_{0\alpha}^{00(\gamma)}(R) - \mathcal{C}_{0\alpha}^{00(\gamma)}(R) = \frac{2\pi}{R}\sum_{\beta=1}^{s}\rho_\beta \int_0^\infty dt\, t\, \mathcal{H}_{0\beta}^{00(\gamma)}(t) \int_{|t-R|}^{t+R} ds\, s\, \mathcal{C}_{\beta\alpha}^{00}(s) \quad (\alpha = 1 \cdots s) \tag{b.10}$$

$$\mathcal{H}_{0\alpha}^{10(\gamma)}(R) - \mathcal{C}_{0\alpha}^{10(\gamma)}(R) = \frac{2\pi}{R}\sum_{\beta=1}^{s-1}\rho_\beta \int_0^\infty dt\, t\, \mathcal{H}_{0\beta}^{10(\gamma)}(t) \int_{R-t}^{t+R} ds\, s\, \mathcal{C}_{\beta\alpha}^{00}(s)$$
$$+ \frac{2\pi}{R}\rho_s \int_0^\infty dt\, t\, \mathcal{H}_{0s}^{11(\gamma)}(t) \int_{R-t}^{t+R} ds\, s\, \mathcal{C}_{s\alpha}^{10}(s) \quad (\alpha = 1 \ldots s-1) \tag{b.11}$$

$$\mathcal{H}_{0s}^{11(\gamma)}(R) - \mathcal{C}_{0s}^{11(\gamma)}(R) = -\frac{2\pi}{R}\sum_{\beta=1}^{s-1}\rho_\beta \int_0^\infty dt\, t\, \mathcal{H}_{0\beta}^{10(\gamma)}(t) \int_{t-R}^{t+R} ds\, s\, \mathcal{C}_{\beta s}^{01}(s)$$
$$+ \frac{2\pi}{R}\rho_s \int_0^\infty dt\, t\, \mathcal{H}_{0s}^{11(\gamma)}(t) \int_{|t-R|}^{t+R} ds\, s\, \mathcal{C}_{ss}^{11}(s) \tag{b.12}$$

The MSA closure conditions are

$$\rho\frac{\mu_\gamma z_\alpha e}{\sqrt{3}} = \int_0^{\sigma_\alpha} dt\, t\, \mathcal{C}_{0\alpha}^{10(\gamma)}(t) \tag{b.13}$$

$$\rho\frac{\mu_\gamma \mu_s}{3} = -\int_0^{\sigma_\alpha} dt\, t^2 \left[\mathcal{C}_{ss;1}^{11(\gamma)}(t) + \mathcal{C}_{ss}^{11(\gamma)}(t)\right] \tag{b.14}$$

with $\mu_\gamma = \mu_s$ for γ=r and $\mu_\gamma = -\lambda/\beta$ for γ=λ. But we observe that for γ=r equations (b.10-14) are the MSA equations for for the unperturbed system (λ=0). This problem is solved elsewhere[29 34]

When γ=λ we have

$$F_{0\alpha}^{mn(\lambda)}(R) = -\frac{\lambda}{\rho\mu_s} F_{0\alpha}^{mn(\gamma)}(R) \quad ((m,n) = (10);(11)), \tag{b.15}$$

The correlation functions have coefficients

$$h_{o\alpha}^{101(\lambda)}(R\ ) = -(\lambda/\beta\ \mu_s)\ h_{s\alpha}^{101}\ (R\ ) \qquad \alpha=1,..,s-1$$
$$h_{o\alpha}^{110(\lambda)}(R\ ) = -(\lambda/\beta\ \mu_s)\ h_{ss}^{110}\ (R\ )$$
$$h_{o\alpha}^{112(\lambda)}(R\ ) = -(\lambda/\beta\ \mu_s)\ h_{ss}^{112}\ (R\ )$$

(b.16)

The case of the pure dipolar fluid is obtained from this result by setting the ionic concentration equal to zero.

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REFERENCES

1) J.Holtsmark, Ann.Phys. (Leipzig),58,1072(1919).

2) H.Margenau, Phys.Revs.,40,387(1932).

3) T.Morita,Progr.Theor.Phys.23,1211,(1960).

4) C.A.Iglesias,Phys.Revs. A27,2705,(1983).

5) C.A.Iglesias,J.L.Lebowitz and D.MacGowan Phys.Revs. A28,1667,(1983).

6) A.Alastuey,C.A.Iglesias,J.L.Lebowitz and D.Levesque,Phys.Revs. A30, 2537,(1984).

7) C.A.Iglesias,J.L.Lebowitz and E.L.Pollock,Phys.Revs. A30,2001,(1984).

8) F.Lado and J.W.Dufty,Phys.Revs. A36,2333,(1987).

9) F.Lado,Phys.Revs. A34,4131,(1986),A36,313,(1987).

10) Y.Rosenfeld,Phys.Revs. A25,1206,(1982).

11) Y.Rosenfeld,Phys.Revs. A26,3622,(1982).

12) Y.Rosenfeld and L.Blum,J.Phys.Chem. 89,5149,(1985).

13) Y.Rosenfeld and L.Blum,J.Chem.Phys. 85,1556,(1986).

14) L.Onsager,J.Phys.Chem. 63,189,(1939).

15) L.Blum and A.J.Torruella,J.Chem.Phys. 56,303,(1972).

16) L.Blum and F.Vericat,in 'The Chemical Physics of Solvation',R.R.Dogonadze E.Kalman, A.A.Kornyshev and J.Ulstrup Editors,Elsevier Publ.Co. Amsterdam, 1985

17) A.R.Edmonds,'Angular Momentum in Quantum Mechanics',Princeton University Press,New Jersey,1957.

18) B.Jancovici,Personal communication, see also ref.5

19) E.Lieb and H.Narnhofer,J.Stat.Phys. 12,2716,(1975) and Ph.Choquard in ,'Strongly Coupled Plasmas ',Edited by G.Kalman

20) Y.Rosenfeld,J.Stat.Phys. 37,215,(1984)

21) Y.Rosenfeld and W.M.Gelbart,J.Chem.Phys.,81,4574,(1974)

22) Y.Rosenfeld,Phys.Revs. A32,1834,(1985)

23) Y.Rosenfeld,Phys.Revs. A33,2025,(1986)

24) Y.Rosenfeld,Phys.Revs. A35, 938,(1987)

25) Y.Rosenfeld,'Comments on the Gaussian approximation for the electric microfield distribution in multicomponent plasmas',to be published

26) J.P.Hansen and I.R.MacDonald,'Theory of Simple Liquids',Acad.Press, London 1976.

27) J.L.Lebowitz and J.K.Percus, Phys.Revs. 144,251,(1966).

28) L.Blum, J.Chem.Phys.58,3295,(1973).

29) L.Blum, J.Stat.Phys.18,451,(1978).

30) E.Waisman and J.L.Lebowitz, J.Chem.Phys.52,430,(1970),56,3086,(1971)

31) L.Blum, Mol.Phys.30,1529,(1975).

32) M.S.Wertheim, J.Chem.Phys.55,4291,(1971).

33) F.Vericat and L.Blum , J.Stat.Phys.22,593,(1980).

34) L.Blum and D.Q.Wei, J.Chem.Phys.87, 555,(1987).

D.Q.Wei and L.Blum, J.Chem.Phys.87,2999,(1987).

D.Q.Wei and L.Blum, J.Phys.Chem.,91,4342,(1987).

FIGURE CAPTIONS

Figure 1:

Distance of closest approach between a convex test particle and hard spherical molecules.

Figure 2:

Self energy of Onsager objects immersed in a perfect conductor.

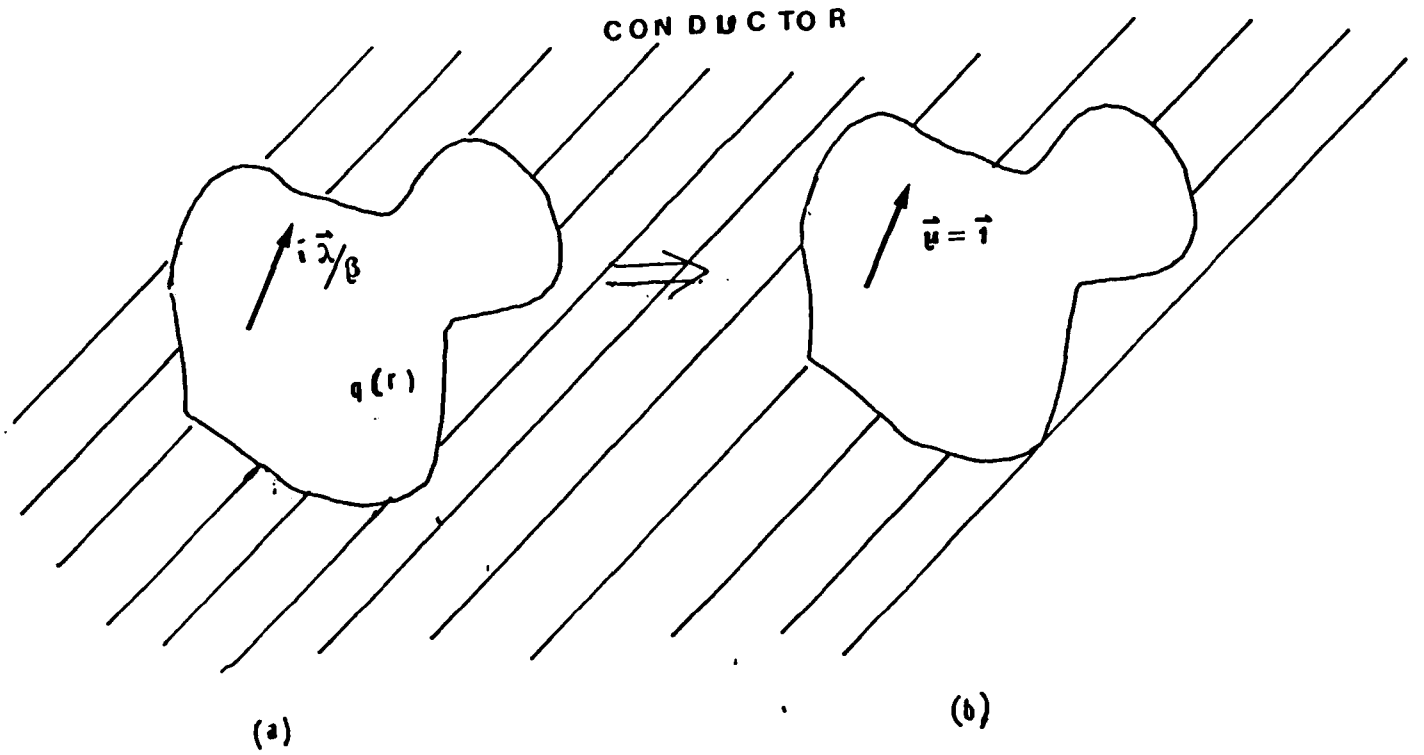
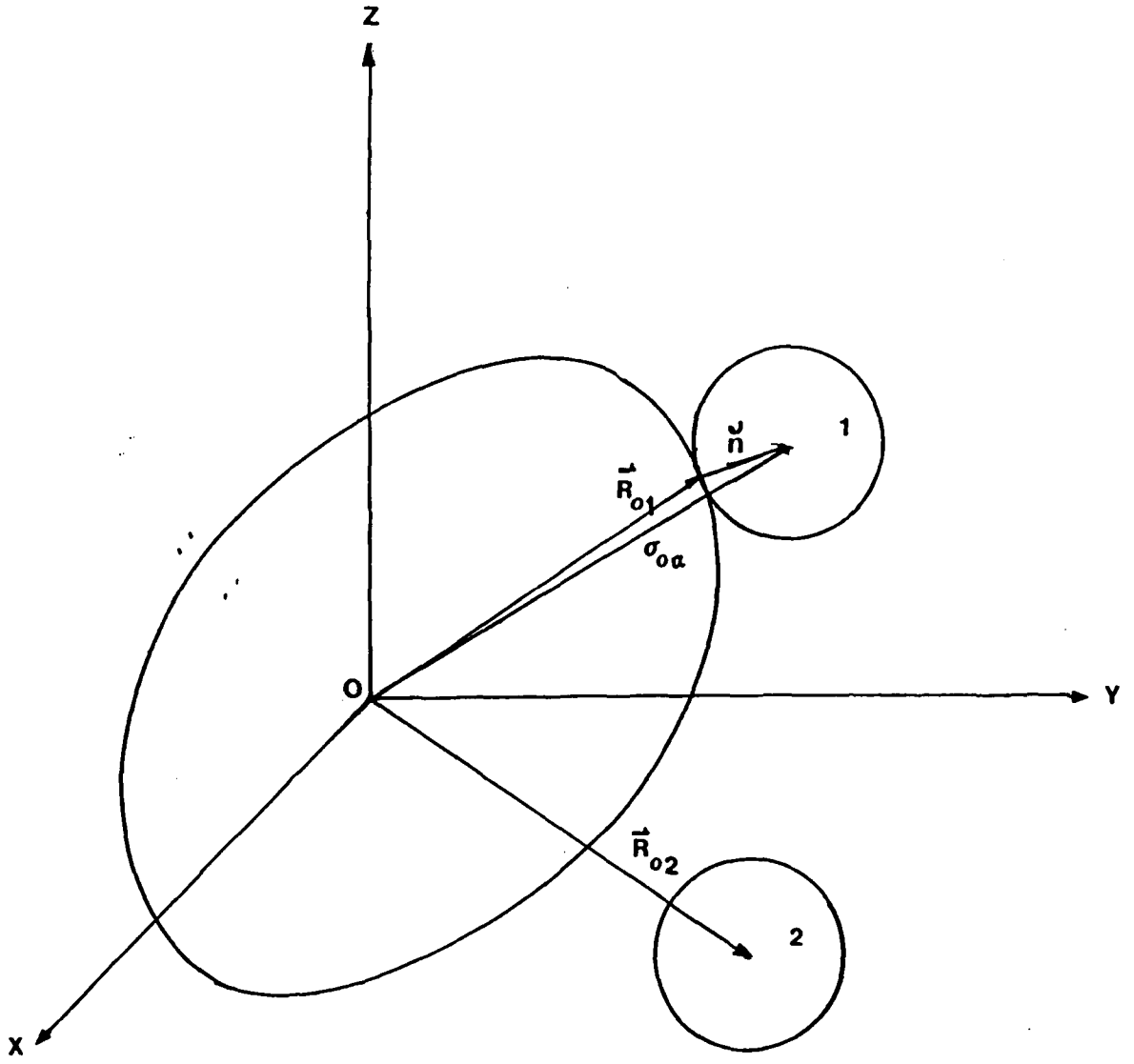


FIGURE 2.


Z
Y
X
O
1
2
$\vec{n}$
$\vec{R}_{01}$
$\sigma_{0\alpha}$
$\vec{R}_{02}$